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M_J and collision energy dependent attenuation of Rg (^{3}P$_2$) by CF$_3$Br

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Abstract. The total attenuation cross-section of Rg (^{3}P$_2$) (Rg = Ar, Kr) by the collision with CF$_3$Br is measured as a function of the magnetic sub level M_J of Rg (^{3}P$_2$) and the collision energy. For Ar (^{3}P$_2$), the attenuation process indicates a M_J dependence, in particular, the cross-section of the $M_J = 0$ state is lower compared with that for other states. On the other hand, Kr (^{3}P$_2$) shows no M_J dependent attenuation.

PACS. 34.50.Gb Electronic excitation and ionization of molecules; intermediate molecular states (including lifetimes, state mixing, etc.)

1 Introduction

The reaction of a metastable rare gas atom with small molecules has been investigated for a long time. In our laboratory, remarkable steric effects have been revealed, especially the dependence on molecular orientation, by means of an electric hexapole method [1–5]. On the contrary, the dependence on the magnetic sub level M_J has remained an unresolved problem. Since metastable rare gas atoms have an open-shell electronic structure, $np^5(n+1)s^1$, the intermolecular interaction depends not only on the molecular orientation but also on the magnetic sub level M_J of the rare gas atoms which is related to the configuration of p-orbital of the rare gas atoms. It is interesting to know how the inner p-orbital of the metastable rare gas atoms, shielded by the outer extended s-orbital, affects the reaction mechanisms.

In the present study, the total attenuation cross-section of Rg (^{3}P$_2$) (Rg = Ar and Kr) by the collision with CF$_3$Br was measured as a function of the collision energy and for selected M_J states. A remarkable M_J dependence of the attenuation was observed for Ar (^{3}P$_2$) by CF$_3$Br, while no M_J dependence was observed for the attenuation of Kr (^{3}P$_2$). It is proposed that the M_J dependence of the attenuation of Ar (^{3}P$_2$) is partly due to the collisional M_J conversion among the five M_J states that favors the transition to the $M_J = 0$ state from other M_J states.

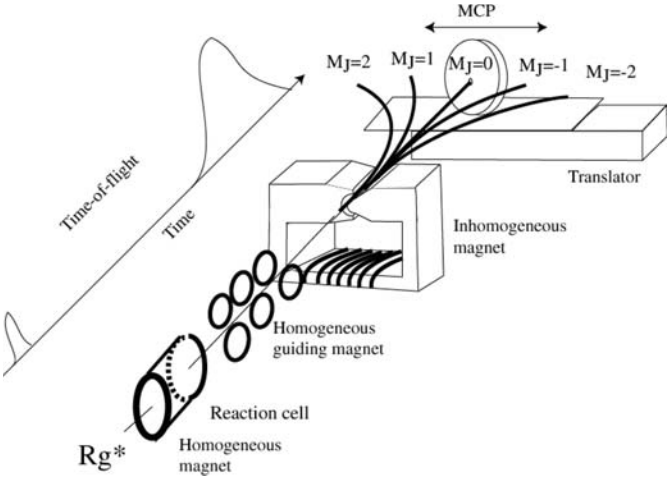

Fig. 1. A schematic view of the experimental apparatus.

2 Experiment

Figure 1 shows a schematic view of the experimental apparatus. The metastable rare gas beam, Rg (^{3}P$_{0,2}$) (Rg = Ar and Kr) was produced by a pulsed glow discharge with a pulse width of 75 μs. The discharge was ignited by a pulsed grid voltage that determines the origin for the time-of-flight measurement with a flight length of 100 cm. The produced metastable rare gas beam is passed through a 10 cm long reaction cell, filled with CF$_3$Br and located in a homogeneous magnetic field of 1000 G, whose direction is set to be parallel to the direction of Rg (^{3}P$_{0,2}$) beam velocity. The CF$_3$Br gas was injected into the reaction cell by a pulsed valve with a pressure of 0.6 Torr. The conductance of the reaction cell was designed to have a time constant of 125 ms for the evacuation. This condition permits the pressure of CF$_3$Br to be maintained at a constant value of $\sim 10^{-4}$ Torr during the 1 ms pulse width of Rg (^{3}P$_{0,2}$) beam which passes through the cell with a time delay of 120 ms after the CF$_3$Br gas injection. It is necessary to

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avoid the mixing of M_J states after the reaction in the field free region between the reaction cell and an inhomogeneous magnetic field. This was done by adiabatically changing the direction of magnetic field toward the direction of an inhomogeneous magnetic field by means of a series of guiding magnetic fields of 200 G. After having passed through the cell, the surviving Rg ($^3P_{0,2}$) that has not reacted with CF_3Br was introduced into the inhomogeneous magnetic field (Stern-Gelrach type) through a 0.3 mm ϕ collimating slit to analyze the population of M_J states under the collision energy resolved condition. The Stern-Gelrach type selector has been used for experiments on open shell atoms, such as metastable rare gas atoms [6] and simple free radicals [7]. The inhomogeneous magnetic field was operated as a 40 ms-width pulse and was activated before the ignition of the glow discharge. The Rg ($^3P_{0,2}$) beam deflected by the inhomogeneous magnetic field was detected by a MCP detector through a slit of 0.3 mm. The slit position was scanned with a step of 0.12 mm by a motor driven translator. The ratio of the Rg ($^3P_0$) relative to the Rg ($^3P_2$) was determined to be negligible (less than 3%) from the decrease of the Rg (^3P) intensity on beam axis by activating the inhomogeneous magnetic field.

3 Results and discussion

3.1 M_J state- and collision energy resolved total attenuation cross-section

Figures 2a and 2b show the time-of-flight spectra of Ar ($^3P_2$) measured at each detector position for two experimental conditions: an empty reaction cell and filled with CF_3Br. The pulsed Ar ($^3P_2$) beam was separated in their five magnetic sub levels by the inhomogeneous magnetic field. The separation increases as the velocity slows.

The collision energy dependence of the total attenuation cross-section at each velocity and the M_J state, $\sigma(v, M_J)$, was determined by the following equation

$$\sigma(v, M_J) \propto -\ln\left(\frac{I_{v,M_J}(\text{with } CF_3Br)}{I_{v,M_J}(\text{without } CF_3Br)}\right) \tag{1}$$

where I_{v,M_J} is the flux of Ar ($^3P_2$) in the magnetic sub level of M_J with velocity v after having passed through the reaction cell under the two conditions, i.e., empty reaction cell and filled with CF_3Br. Figure 2c shows the collision energy dependence of the total attenuation cross-section for Ar ($^3P_2$)+CF_3Br collision. The cross-section decreases as the collision energy increases.

The plots of the total attenuation cross-section along the collision energy for each M_J state in Ar ($^3P_2$)+CF_3Br collision are shown in Figure 3. At a glance, it can be seen that the cross-section of $M_J = 0$ state is much lower than that for the other M_J states in the region where the collision energy is lower than 0.14 eV. For $|M_J| = 2$ states, the cross-section of the positive M_J is slightly smaller than that for the negative M_J state. On the other hand, no difference was observed between the $|M_J| = 1$ states.

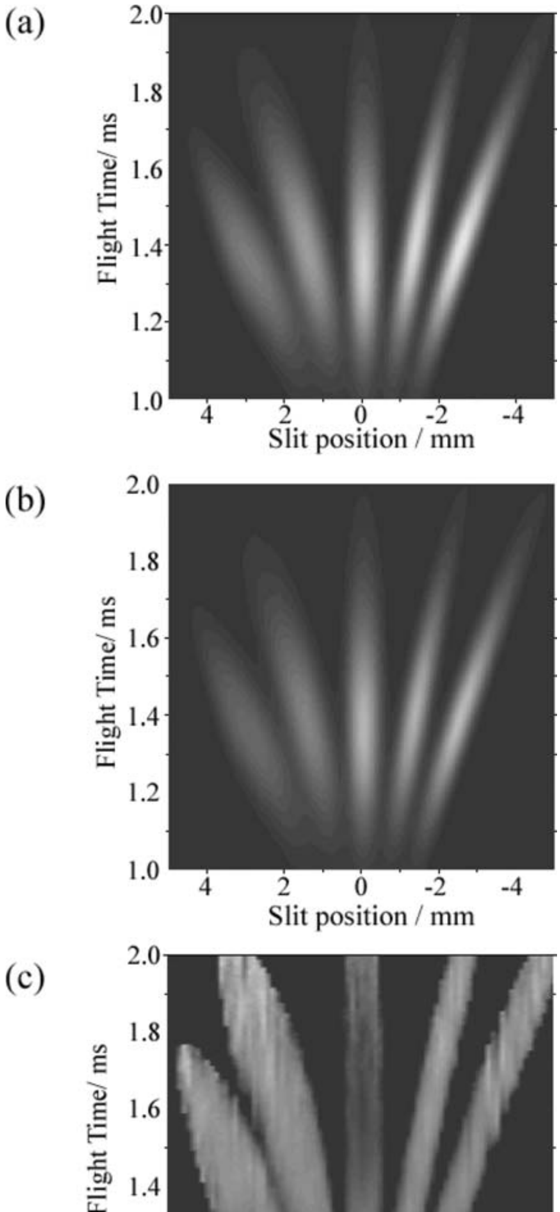

Fig. 2. Time-of-flight spectra of Ar ($^3P_2$) under the two experimental conditions; (a) without CF_3Br; (b) with CF_3Br gas; (c) the collision energy dependence of the total attenuation cross-section, $\sigma(v, M_J)$, for each M_J state determined by equation (1).

In the same manner, the M_J dependent attenuation cross-section for Kr ($^3P_2$) was obtained as the function of the collision energy. This is shown in Figure 4. In contrast with Ar ($^3P_2$), no M_J dependence was observed.

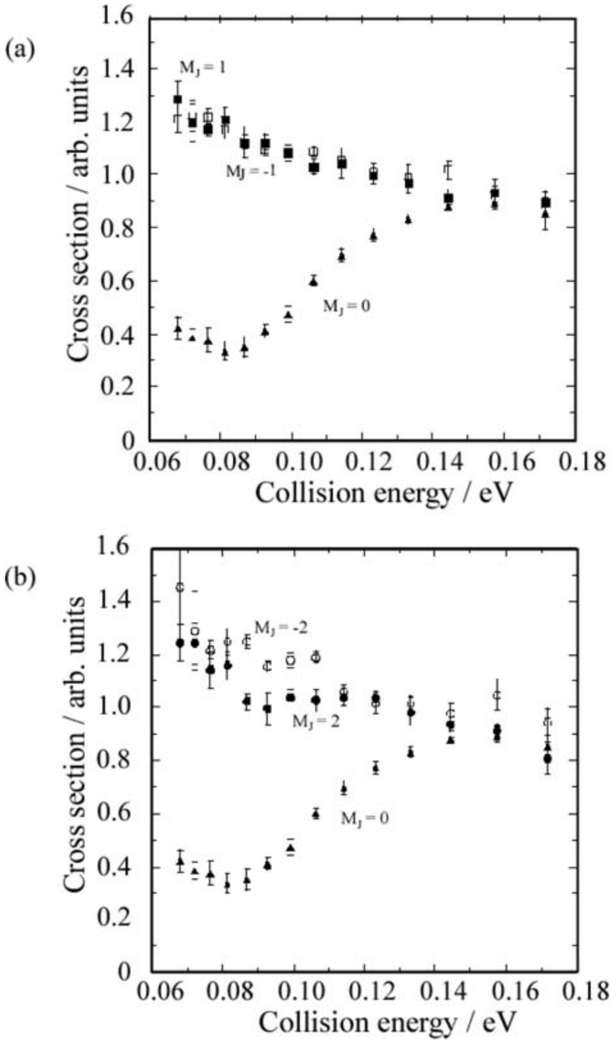

Fig. 3. The plots of the attenuation cross-section of Ar ($^3P_2$)+ CF_3Br reaction along the collision energy for each M_J state (a) $|M_J| = 1$, (b) $|M_J| = 2$; $M_J = 2$ (●), $M_J = 1$ (■), $M_J = 0$ (▲), $M_J = -1$ (□), $M_J = -2$ (○).

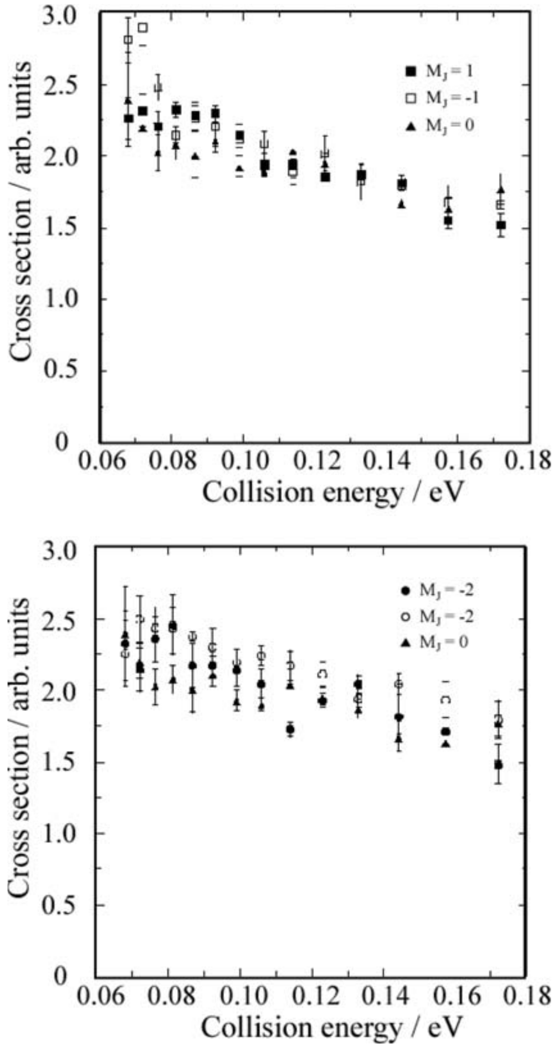

Fig. 4. The plots of the attenuation cross-section of Kr ($^3P_2$)+ CF_3Br reaction along the collision energy for each M_J state (a) $|M_J| = 1$, (b) $|M_J| = 2$; $M_J = 2$ (●), $M_J = 1$ (■), $M_J = 0$ (▲), $M_J = -1$ (□), $M_J = -2$ (○).

4 Discussion

The cross-section measured in the present study is the total attenuation cross-section. Therefore, the observed cross-section includes the following three processes

(a) $Rg^*(M_J = m) + CF_3Br \rightarrow Rg + CF_3Br^*$

(b) $Rg^*(M_J = m) + CF_3Br \rightarrow Rg^*(M_J \neq m) + CF_3Br$

(c) $Rg^*(M_J = m) + CF_3Br \rightarrow Rg^*(M_J = m) + CF_3Br.$

The process (a) is the de-excitation, in which the metastable Rg* is removed by the quenching to the ground state with energy transfer to the CF_3Br and by the reaction with CF_3Br. The process (b) corresponds to the M_J conversion collision, and the last one (c) is the elastic collision. Although a rather large total de-excitation cross-section of Ar* and Kr* by CF_3Br has been reported; 69 A^2 for Ar* and 145 A^2 for Kr* [14], we predict a rather large contribution from the elastic cross-section for the present systems. At this stage, unfortunately, it is difficult to distinguish the above three processes because of the limitation of the experimental technique. Since it is well-known that the interaction potential for Rg* is well approximated by that of the corresponding alkali metal, the elastic cross-section is expected to be determined mainly by the interaction with the outer *s*-orbital. Therefore, the elastic cross-section is expected to have little M_J-state dependence. In addition, the quantum glory undulation is expected to be efficiently blurred by thermal motion of the target gas in the present study. These situations mean that the elastic cross-section contributes only as a monotonic offset signal in the observed total attenuation cross-section. In other words, it is reasonable to assume that the M_J-state dependence appearing in the total attenuation cross-section corresponds to the M_J-state dependence of the total de-excitation cross-section and that the M_J conversion collision is strongly related to the inner *p*-orbital. Based on this assumption, we discuss the M_J-state

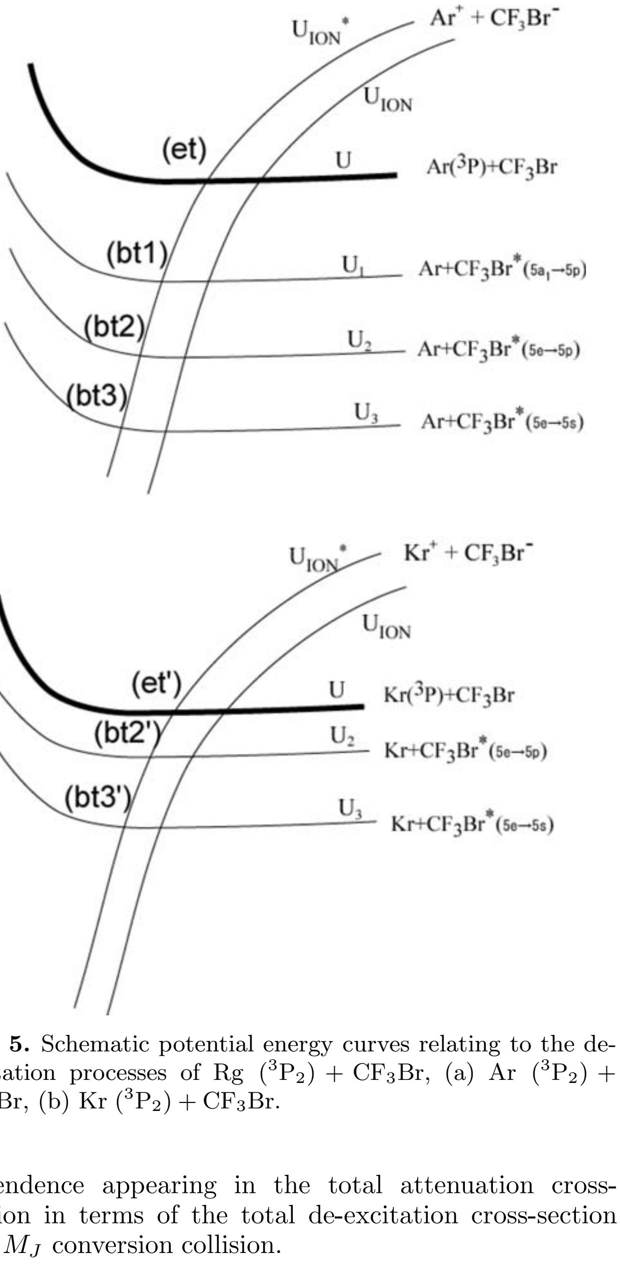

Fig. 5. Schematic potential energy curves relating to the de-excitation processes of Rg ($^3P_2$) + CF_3Br, (a) Ar ($^3P_2$) + CF_3Br, (b) Kr ($^3P_2$) + CF_3Br.

dependence appearing in the total attenuation cross-section in terms of the total de-excitation cross-section and M_J conversion collision.

4.1 Overview of de-excitation processes

Although the main exit channels for the de-excitation processes have not been identified, it would reasonable to expect neutral dissociation via the energy transfer processes, because of the small branching fraction for the chemi-ionization and the excimer formation; 0.02 and 0.03, respectively [15,16]. The excited states of CF_3Br have been widely investigated by means of various methods [8–13]. A schematic multi-potential energy surface for the Ar ($^3P_2$) + CF_3Br reaction is shown in Figure 5a. The energetically accessible neutral dissociation channels are as follows; (1) $CF_3{}^*$ formation from the Ar + CF_3Br^{*1} surface designated as U_1, (2) CF_3 formation from Ar + CF_3Br^{*2} surface, U_2, and (3) CF_3 formation from the Ar + CF_3Br^{*3} surface, U_3. The CF_3Br^{*1} state is characterized by the excitation of the $5a_1$ orbital localized in the C–Br bond. On the other hand, the CF_3Br^{*2} and CF_3Br^{*3} states are characterized by the excitation of the $5e$ orbital that is the lone pair electron of Br. The schematic potential curves for the Kr ($^3P_2$) + CF_3Br are shown in Figure 5b. For the Kr ($^3P_2$), only the excitations to the CF_3Br^{*2} and CF_3Br^{*3} states are energetically accessible. In both Rg ($^3P_2$) cases, the de-excitation processes should proceed via the electron transfer (et) and the subsequent back-electron transfer (bt1)–(bt3). In order to understand the M_J dependence of the de-excitation processes, we must consider the M_J dependence for the non-adiabatic transition probabilities in the electron transfer (et) and in the subsequent back-electron transfer (bt1)–(bt3).

Although the ^3P_J states are the eigenstates of the asymptotic Hamiltonian where Rg* and CF_3Br are infinitely separated, the pure $|J, J_Z, L, S\rangle$ state can no longer be the eigenstates of the Hamiltonian where the reactants have interacted. When the molecules approach along the quantization axis, the ^3P_J states split into the perturbed states, which are originally the pure states of the $|L, S, L_Z, S_Z\rangle$ basis. In this case, the ^3P_J states can be expressed by using the $|L, S, L_Z, S_Z\rangle$ basis as follows [17]

$$\begin{aligned}
|2,2\rangle_{J,J_Z} &= |1,1\rangle_{L_Z,S_Z}\\
|2,1\rangle_{J,J_Z} &= \sqrt{1/2}\,|1,0\rangle_{L_Z,S_Z} + \sqrt{1/2}\,|0,1\rangle_{L_Z,S_Z}\\
|2,0\rangle_{J,J_Z} &= \sqrt{1/6}\,|1,-1\rangle_{L_Z,S_Z} + \sqrt{2/3}\,|0,0\rangle_{L_Z,S_Z}\\
&\quad + \sqrt{1/6}\,|-1,1\rangle_{L_Z,S_Z}\\
|2,-1\rangle_{J,J_Z} &= \sqrt{1/2}\,|0,-1\rangle_{L_Z,S_Z} + \sqrt{1/2}\,|-1,0\rangle_{L_Z,S_Z}\\
|2,-2\rangle_{J,J_Z} &= |-1,-1\rangle_{L_Z,S_Z}\\
|0,0\rangle_{J,J_Z} &= \sqrt{1/3}\,|1,-1\rangle_{L_Z,S_Z} - \sqrt{1/3}\,|0,0\rangle_{L_Z,S_Z}\\
&\quad + \sqrt{1/3}\,|-1,1\rangle_{L_Z,S_Z}.
\end{aligned} \tag{2}$$

4.2 Electron transfer

As described above, the de-excitation mechanism can be mainly attributed to the excitation to the U_1, U_2 and U_3 states through the non-adiabatic transitions at the crossing points; (et), (bt1), (bt2) and (bt3). First we consider the electron transfer process from the initial surface U to the ion-pair surface U_{Ion} at the crossing point (et).

For the metastable rare gas, it is expected that the interaction between the outer extended s-orbital and the inner p-orbital is weak. In such a case, the angular momentum L_Z should be conserved in the course of electron transfer from the 4s (for Ar) and 5s (for Kr) electron of Rg ($^3P_2$) to the Rydberg orbital of CF_3Br at the crossing point (et), whereas, $S_Z = s_Z(3p) + s_Z(4s)$ is changed by $\Delta S_Z = s_Z(4s) = \pm 1/2$. As a result, the angular momentum $L_Z + s_Z(3p)$ for the ion core of Rg^+ should be conserved in the course of the electron transfer process. By using the quantum number of $\Omega = L_Z + s_Z(3p)$, it was found that the potential surface U for the Rg* states with $|M_J| = 2$ are crossed with only the Rg^+ ($^2P_{3/2}$) ion-pair surface (U_{Ion}) with $|\Omega| = 3/2$. On the other hand, the potential surface U for $M_J = 0$ state is crossed with only the

Rg$^+$ ($^2\mathrm{P}_{1/2}$) ion-pair surface (U^*_{Ion}) with $|\Omega| = 1/2$. For the $|M_J| = 1$ states, two ion-pair surfaces Rg$^+$ ($^2\mathrm{P}_{3/2}$) (U_{Ion}) and Rg$^+$ ($^2\mathrm{P}_{1/2}$) (U^*_{Ion}) can be crossed with the initial surface U. Generally speaking, the back-electron transfer probabilities should have little collision energy dependence, because the relative velocity at the crossing points (bt1)–(bt3) are mostly determined by the acceleration on the ion-pair surface. Therefore, the collision energy dependence of the de-excitation cross-section would be mainly determined by the electron transfer processes that occur at the different crossing points depending on the M_J states. From this reason, the different $|M_J|$ states should have a different collision energy dependence, if the L_Z is conserved in the course of electron transfer. For the Ar ($^3\mathrm{P}_2$), we can see the different collision energy dependence for the different $|M_J|$ states. For the Kr ($^3\mathrm{P}_2$), on the other hand, the collision energy dependence seems to be almost identical for all M_J states. From these results, it is suggested that L_Z is conserved for the Ar ($^3\mathrm{P}_2$) in the course of electron transfer, while L_Z is not conserved for the Kr ($^3\mathrm{P}_2$). Indeed, no M_J dependence of the attenuation cross-section was observed for the CF$_3$H + Kr ($^3\mathrm{P}_2$) reaction system.

4.3 Back-electron transfer

As the second step of the energy transfer process, we must consider the M_J dependence for the back-electron transfer process. The back-electron transfer should be controlled by the orbital overlap of the $3p$ (for Ar) and $4p$ (for Kr) hole of Rg$^+$ with the $5e$ and $5a_1$ orbitals. Consequently, the directional character of the p-orbital in the ion core of Rg$^+$, L_Z should have a significant effect for the orbital overlap. In addition, since the different $|\Omega|$ states have a different crossing distance for the back-electron transfer, the value of $|\Omega|$ should also have a significant effect on the orbital overlap efficiency.

The directional character of the p-orbital for each M_J state should be clarified using the expression based on the $|L_Z(ion), \Omega\rangle$ basis

$$\begin{aligned}
|2,2\rangle_{J,J_Z} &= |1,3/2\rangle_{L_Z,\Omega} \\
|2,1\rangle_{J,J_Z} &= \sqrt{1/2}\,|1,3/2\rangle_{L_Z,\Omega} \text{ (or } |1,1/2\rangle_{L_Z,\Omega}) \\
&\quad + \sqrt{1/2}\,|0,1/2\rangle_{L_Z,\Omega} \\
|2,0\rangle_{J,J_Z} &= \sqrt{1/6}\,|1,1/2\rangle_{L_Z,\Omega} + \sqrt{2/3}\,|0,\pm 1/2\rangle_{L_Z,\Omega} \\
&\quad + \sqrt{1/6}\,|-1,-1/2\rangle_{L_Z,\Omega} \\
|2,-1\rangle_{J,J_Z} &= \sqrt{1/2}\,|0,-1/2\rangle_{L_Z,\Omega} \\
&\quad + \sqrt{1/2}\,|-1,-3/2\rangle_{L_Z,\Omega} \text{ (or } |-1,-1/2\rangle_{L_Z,\Omega}) \\
|2,-2\rangle_{J,J_Z} &= |-1,-3/2\rangle_{L_Z,\Omega}. \qquad (3)
\end{aligned}$$

From a simple consideration of the orbital symmetry, we can deduce the efficiency of the orbital overlap between the $3p$ (for Ar), $4p$ (for Kr) hole of Rg$^+$ and the MO of CF$_3$Br. For the collinear approach without an impact parameter, the $L_Z = 0$ component is expected to be efficient for the back-electron transfer with the $5e$ orbital, whereas the $L_Z = 1$ component favors the back-electron transfer with the $5a_1$ orbital. Figure 4 indicates that the back-electron transfer (bt1) with the $5a_1$ orbital is dominant for Ar ($^3\mathrm{P}_2$), whereas the back-electron transfers (bt2′, bt3′) only occur with the $5e$ orbital for Kr ($^3\mathrm{P}_2$). From equation (3), it is expected that the de-excitation cross-section of $M_J = 0$ state is smaller for Ar ($^3\mathrm{P}_2$), and the de-excitation cross-section of $M_J = 0$ state is larger for Kr ($^3\mathrm{P}_2$). For the Ar ($^3\mathrm{P}_2$) case, the smaller attenuation cross-section observed for the $M_J = 0$ state might be partly due to this favorable selectivity of the $L_Z = 1$ component in the back-electron transfer (bt1) with the $5a_1$ orbital. On the contrary, for Kr ($^3\mathrm{P}_2$) case, we could not experimentally observe a favorable attenuation cross-section for the $M_J = 0$ state. Since the CF$_3$Br is randomly oriented and the back-electron transfers take place at a long intermolecular distance with the impact parameters in the actual collision, the M_J selectivity must be smeared out.

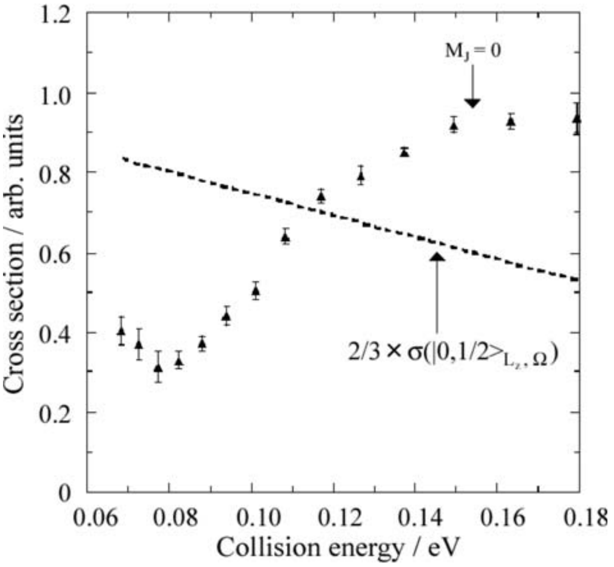

Fig. 6. (▲) The cross-section for the $|2,0\rangle_{J,J_Z}$ state in the reaction of Ar ($^3\mathrm{P}_2$) + CF$_3$Br. Dashed line: the contribution of the $|0,1/2\rangle_{L_Z,\Omega}$ component in the $|2,0\rangle_{J,J_Z}$ state estimated by the factor of $(4/3)[\sigma(|2,1\rangle_{J,J_Z}) - 0.5\sigma(|2,2\rangle_{J,J_Z})]$. The estimated $|0,1/2\rangle_{L_Z,\Omega}$ component in the $|2,0\rangle_{J,J_Z}$ state becomes larger than the cross-section itself for the $|2,0\rangle_{J,J_Z}$ state.

If we assume the conservation for the angular momentum L_Z and Ω in the course of the back-electron transfer process, the relative reactivity among the M_J states can be estimated by using equation (3). In such a case, the cross-section for the $|0,1/2\rangle_{L_Z,\Omega}$ component, $\sigma(|0,1/2\rangle_{L,\Omega})$ can be estimated as follows:

$$\sigma(|0,1/2\rangle_{L,\Omega}) = 2[\sigma(|2,1\rangle_{J,J_Z}) - 0.5\sigma(|2,2\rangle_{J,J_Z})].$$

In addition, the contribution of the $|0,1/2\rangle_{L_Z,\Omega}$ component in the $|2,0\rangle_{J,J_Z}$ state also can be estimated by the factor of $(2/3)\sigma(|0,1/2\rangle_{L,\Omega})$. The estimated contribution of the $|0,1/2\rangle_{L_Z,\Omega}$ component is shown in Figure 6 as a dashed line. It was found that the estimated $|0,1/2\rangle_{L_Z,\Omega}$

component in the $|2,0\rangle_{J,J_Z}$ state became larger than the cross-section of the $|2,0\rangle_{J,J_Z}$ state itself. That is to say, the experimental attenuation cross-section for the $|2,0\rangle_{J,J_Z}$ state is much lower than the estimated one. This result strongly indicates that the L_Z component is not perfectly conserved during the collision processes. Unfortunately, it is difficult to distinguish between the M_J conversion collision and the M_J dependent de-excitation in the present study, because the M_J state-selection before the collision is not prepared in the present study. However, in order to explain the lower attenuation cross-section of the $M_J = 0$ state, we must assume a favorable collisional M_J conversion to the $M_J = 0$ state from the other M_J states. That is to say, the favorable M_J conversion to the $M_J = 0$ state decreases the apparent attenuation cross-section for the $M_J = 0$ state. In other words, the transition of $|L_Z| = 1 \rightarrow L_Z = 0$ for the inner p-orbital of Ar ($^3P_2$) must occur in the course of the collision processes. For a more quantitative understanding, the preparation of an oriented Rg (^{3}P) beam before the collision is necessary. Moreover, the combination of an oriented molecular beam and an oriented Rg (^{3}P) beam should be a powerful tool to resolve steric effects on the de-excitation process. Such a study is now in progress. It will enable a quantitative answer for the selectivity of M_J to be given.

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